

CO₂ UTILIZATION FOR MECHANOCHEMICAL CARBONATION OF CELESTINE

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Abstract

Natural celestine (SrSO₄) has been successfully transformed into strontianite (SrCO₃) via fast one-step mechanochemical carbonation utilizing gaseous CO₂. The process was realized in the environment enriched with LiOH or NaOH additives. The mixtures were milled in a high-energy planetary ball mill for 40 min. The phases formed during the milling were characterized by different characterization techniques, such as X-ray diffraction (XRD) and infrared spectroscopy (FT-IR). The presence or absence of carbon or sulphur in the products was confirmed by a CHNS analysis.

Keywords: celestine, strontianite, mechanochemical processing, CO₂

1 INTRODUCTION

In the last years, the interest in the study of CO₂ utilization is growing due to the real risk of global warming caused by increasing concentrations of this greenhouse gas in the atmosphere. Recovering CO₂ from the exhaust of power plants [1] and converting it into useful products would help to lower its content in the atmosphere.

Mineral carbonation is a process where CO₂ is chemically combined with minerals forming stable carbonates. It proceeds under ambient conditions, however, very slowly [2]. Therefore, the minerals need to be activated to enhance the kinetics and economy of the carbonation process.

Mechanical activation enables the change of solid-state properties by size reduction, creation of lattice imperfections and increase of the surface area, all of which have a positive influence on the kinetics of the carbonation process. By the concept of mineral carbonation, the process of carbonates formation during milling in the presence of CO₂ atmosphere could be defined as mechanochemical carbonation (mechanocarbonation).

Celestine is the principal strontium mineral mined for the production of SrCO₃ by the commercial black ash and double decomposition processes. Besides these two methods, SrSO₄ can also be converted into SrCO₃ by a direct mechanochemical route using Na₂CO₃ [3-5] or (NH₄)₂CO₃ [6]. Zhang and Saito [7] also obtained SrCO₃ indirectly (by exposure to air) using carbonation of Sr(OH)₂ synthesised mechanochemically from SrSO₄ and NaOH. Using hydroxides or hydrates as precursors accelerates the chemical reaction, and this method is also called “soft mechanochemical method” [8].

The aim of the present work is to investigate the carbonation characteristics of SrSO₄ realized via high-energy milling in a gaseous CO₂ environment in the presence of LiOH and NaOH additives.

2 EXPERIMENTAL PART

2.1 Mechanochemical carbonation

In the experimental studies, reagent-grade SrSO₄ (5 g), LiOH or NaOH (20% excess, 1.56 g or 2.61 g) and CO₂ gas were used.

The milling experiments were performed in a laboratory planetary mill Pulverisette 6 for 40 min at 500 rpm using a grinding chamber (250 cm³ in volume) and balls (10 mm in diameter) made of tungsten carbide. At the end, the milled solids were washed with distilled water.

When used, CO₂ was flushed once into the reaction chamber prior to the experiment to ensure that the air was expelled. The duration of CO₂ flushing was 3 min at a pressure of 0.5 MPa (gas flow rate of 0.1 L/min), and the temperature was maintained at 25±1 °C.

2.2 Characterization

The powder X-ray diffraction (XRD) data were collected over an angular range $20 < 2\theta < 50^\circ$ with a step size of 0.025° using a Bruker D8 Advance diffractometer working with $\text{CuK}\alpha$ radiation and a scintillation detector working in Bragg-Brentano geometry. The diffraction patterns were treated with the Diffra^{plus}Eva and Topas analysis program, using the ICDD PDF2 database for phase analysis and Rietveld analysis, respectively.

Fourier-transform infrared spectra (FTIR) were measured with a Tensor 29 (Bruker) in the frequency range of $4000\text{--}400\text{ cm}^{-1}$ using the KBr pellet method. KBr was dried before the analysis at 100°C for 1 h.

The total carbon and sulphur content of the milled samples was determined using a CHNS Elementar Vario Macro Cube analyser.

3 RESULTS AND DISCUSSION

The mechanochemical carbonation process was realized in three different ways according to the theoretical reactions (1)–(3) (see Tab. 1). In the first step, SrSO_4 was milled with CO_2 gas according to the reaction (1). In the second step, SrSO_4 was milled with the indicated MOH ($M = \text{Li}$ or Na) compound according to the reactions (2) and (3).

No transformation to SrCO_3 during milling of SrSO_4 in the presence of CO_2 without hydroxide additives is expected due to the high positive Gibbs free energy value (Tab. 1). On the other hand, the formation of the carbonate phase is expected due to the negative Gibbs free energy values of the theoretical reactions (2) and (3), when LiOH or NaOH are used.

Tab. 1 Standard Gibbs free energy changes of the investigated reactions, carbon and sulfur contents of the milled solids.

	Reaction	ΔG_{298}^0 (kJ/mol)	C (%)	S (%)
(1)	$\text{SrSO}_4 (\text{s}) + \text{CO}_2 (\text{g}) = \text{SrCO}_3 (\text{s}) + \text{SO}_3$	+231	0.06	17.53
(2)	$\text{SrSO}_4 + 2\text{LiOH} + \text{CO}_2 = \text{SrCO}_3 + \text{Li}_2\text{SO}_4 + \text{H}_2\text{O}$	-78	6.99	2.49
(3)	$\text{SrSO}_4 + 2\text{NaOH} + \text{CO}_2 = \text{SrCO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	-145	3.45	9.92

Fig. 1 shows the X-ray diffraction patterns of the dry high-energy milled solids, which were prepared according to the reactions (1)–(3). When the reaction (1) was followed, no phase change occurred, SrSO_4 (JCPDS PFD 05-0593) was the major product obtained after milling. According to the XRD results, tracing the reactions (2) and (3), the usage of either LiOH or NaOH in the initial mixture accelerates the mechanochemical carbonation of celestine, however, with slightly different results. In both cases, all diffraction peaks in the spectra can be ascribed to the orthorhombic SrCO_3 but with different space group modification, depending on the type of alkaline carbonate used. Concretely, the *Pm*cn (JCPDS PFD 84-1778) or the *Pn*ma (JCPDS PFD 74-1491) types were observed when LiOH or NaOH were used, respectively.

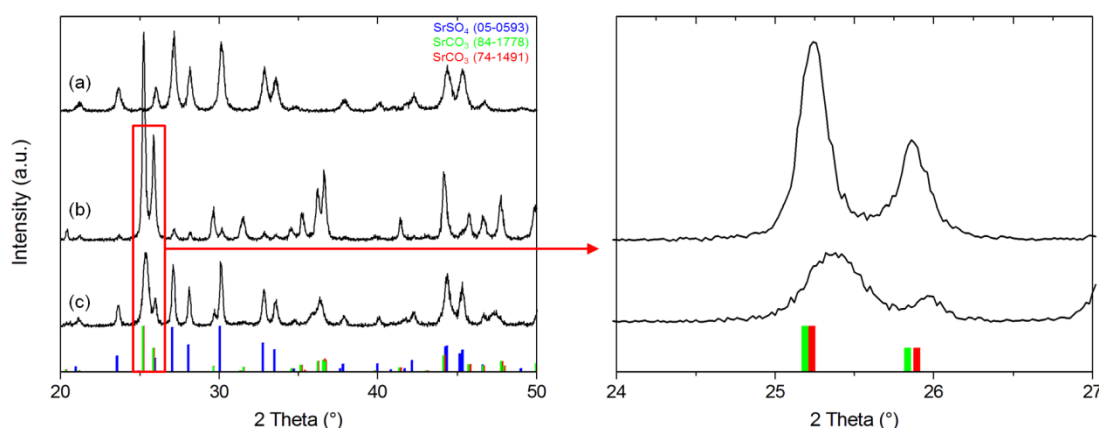


Fig. 1 XRD patterns of solids obtained by high-energy milling of (a) SrSO_4 in a gaseous CO_2 environment in the presence of (b) LiOH and (c) NaOH .

The infrared results correspond well with the XRD analysis, as seen in Fig. 2. In all spectra, the peaks observed in the range of 700-600 cm^{-1} and 1300-950 cm^{-1} are characteristic for the ν_1 , ν_3 and ν_4 vibrations of the SrSO_4 sulphate ion [9-11].

In the first step (reaction (1)), similar to the XRD results (Fig. 1a), no bands related to SrCO_3 were observed. On the other hand, the FT-IR spectra of the solids obtained by milling of SrSO_4 in the CO_2 atmosphere in the presence with hydroxide additives match the XRD results, confirming the SrCO_3 formation. It should be noted, the infrared spectra of carbonate minerals are characterized by a single (antisymmetric stretching vibrations of the undistorted CO_3^{2-} group) or double (asymmetric stretching vibrations of the distorted CO_3^{2-} group) peak in the region of 1550-1350 cm^{-1} [12]. The distortion of this group may occur due to the (i) presence of structural water in hydrated or hydroxylated-hydrate form [13], (ii) metal itself, which is present in the structure or is used as additive during the synthesis [14], and (iii) due to the distorted crystal structure [15]. As can be seen, the observed bands attributed to the carbonate ion in SrCO_3 [10, 11, 16-18] in the range of 1440-1580 cm^{-1} were single or split depending on whether NaOH or LiOH was used as an additive. Interestingly, it seems that the alkaline metal has an influence on the structure of SrCO_3 with respect to the type of the space group setting (*Pnma* or *Pmcn*) and, consequently, on the type of the main CO_3^{2-} band in the infrared spectra.

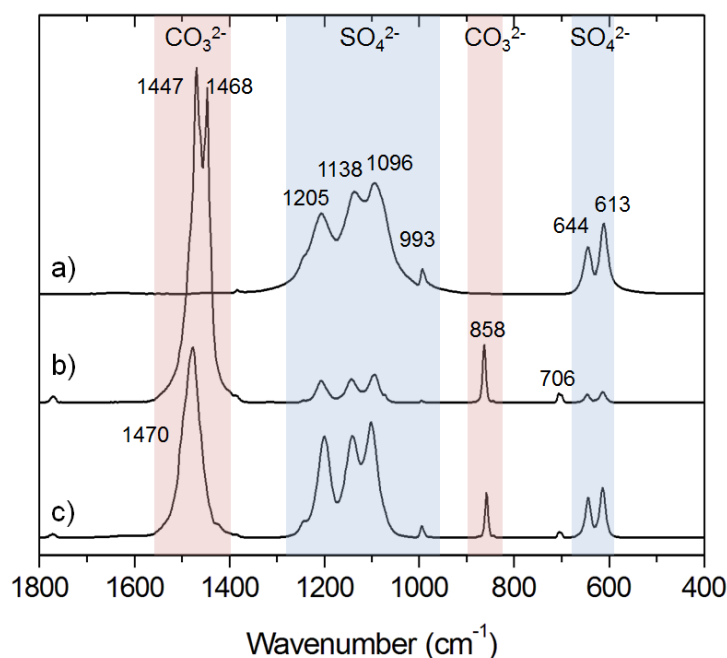


Fig. 2 IR spectra of solids obtained by high-energy milling of (a) SrSO_4 in a gaseous CO_2 environment in the presence of (b) LiOH and (c) NaOH.

In addition to the XRD and FT-IR, the carbon and sulphur analyses (Tab. 1) also confirmed the unsuccessful process of the celestine conversion to SrCO_3 in the absence of hydroxide, as indicated by the small amount of carbon detected in the product. The carbonation of SrSO_4 to SrCO_3 in the presence of LiOH or NaOH is evidenced by the increase in the amount of detected carbon. The carbon content of the milled solid, 6.99 (LiOH) and 3.45% (NaOH), quantifies the degree of the mineral carbonation process, showing that approximately 87% and 43% of initial SrSO_4 was carbonated by high-energy milling, respectively.

4 CONCLUSIONS

The process of carbonation of SrSO_4 by dry high-energy milling in the CO_2 atmosphere was investigated with attention paid to the effect of LiOH and NaOH. In the presence of only CO_2 , the mechanochemical formation of SrCO_3 has not been observed. Direct mechanochemical formation of SrCO_3 was observed during the co-milling of SrSO_4 with MOH ($M=\text{Li}$ or Na) in the CO_2 atmosphere, and it was shown that at least 43% of initial SrSO_4 was mechanochemically carbonated in the presence of NaOH.

According to the type of alkali hydroxide used, strontium carbonate with different space group settings, having single or split carbonate absorption bands, can be obtained. From this study follows, that strontium compounds are also exploitable, besides the generally used magnesium and calcium compounds, in mineral carbon dioxide sequestration processes.

These results support the conclusion that celestine could be used as a raw material for CO₂ sequestration.

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